Hydrophobic photonic crystal fibers

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We propose and demonstrate hydrophobic photonic crystal fibers (PCFs). A chemical surface treatment for making PCFs hydrophobic is introduced. This repels water from the holes of PCFs, so that their optical properties remain unchanged even when they are immersed in water. The combination of a hollow core and a water-repellent inner surface of the hydrophobic PCF provides an ultracompact dissolved-gas sensor element, which is demonstrated for the sensing of dissolved ammonia gas. © 2011 Optical Society of America

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Photonic crystal fibers (PCFs) [1] have attracted considerable interest for a wide range of applications in fiber sensors and optical communications. The air-filled holes in the PCFs can significantly improve optical fiber properties—like endlessly single-mode propagation, photonic bandgap guidance and tailored dispersion—giving rise to new applications [2]. The holes in the PCFs and the bandgap guiding mechanism also open up new opportunities for various functional fibers and compact sensing platforms by the interaction of light with matter (gas, liquid, semiconductor, metal, glass, nanoparticles, etc.) in the holes [3,4]. The nature of the holes in the PCF makes it easy to insert liquids by capillary force or pressure, which is very useful for integrated fiber devices and detecting fluidic samples [5,6]. However, the presence of liquids generally has undesirable effects on light transmission and handling. Having liquid in a PCF will dramatically change its guiding properties and can cause large losses, which seriously limit many applications in liquid or humid environments.

In this Letter, we propose the concept of, and demonstrate, hydrophobic PCFs. A hydrophobic PCF is a microstructured fiber where the surfaces of the holes are modified by hydrophobic molecules without significantly affecting its optical guiding properties. As water cannot wet the inner surface and flow into the holes, such a PCF can work even when the fiber is immersed in aqueous liquids. One of its applications was demonstrated: dissolved-gas sensing in water.

It is well known that capillary forces will pull water into a capillary when the contact angle of the meniscus with the wall is below 90°, as shown in Fig. 1(a). In contrast, the water will be pushed out when the contact angle is larger than 90° [Fig. 1(b)]. A PCF is made from many such parallel holes [Fig. 1(c)]. Fused silica surfaces are naturally more or less covered with hydroxyl (—OH) groups [7]. If the amount of hydroxyl on the surface of the holes is increased [Fig. 1(d)], they become more hydrophilic and fill more quickly with water. However, it has been shown that, if the surface is treated by hexamethyldisilazane (HMDS), the hydroxyl will be replaced by trimethylsilyl (—$OSi(CH_3)_3$) groups [7], as shown in Fig. 1(e). This has recently been applied to our silica aerogel [8]. The surface will become hydrophobic: the contact angle will be larger than 90° and the water cannot enter the holes of the PCF when it is immersed.

The experiment setup shown in Fig. 2 was used to make a PCF hydrophobic. 1 m of PCF was connected to a vacuum pump and a bubbler system. Nitrogen gas bubbled through a liquid accelerated its evaporation and carried the vapor into the fiber. The vacuum pump was used to keep the gas flowing smoothly inside the PCF. The PCF was first treated by exposure to water vapour for one day to maximize the hydroxyl coverage of its inner surfaces. Then the water was replaced with HMDS and the PCF was treated with HMDS vapor for two days to make its inner surfaces hydrophobic.

Two kinds of hydrophobic PCFs were made, one a hollow-core bandgap PCF, as shown in Fig. 2, with a working wavelength range from 1450 to 1600 nm, and the other a solid-core PCF with a core diameter of 3 μm (Fig. 3, inset). The surface modification changed the measured attenuation of the hollow-core bandgap PCF by less than 0.5 dB/m across the working wavelength range. The excess attenuation due to surface modification of the solid-core PCF (Fig. 3) was also low, less than 0.6 dB/m,

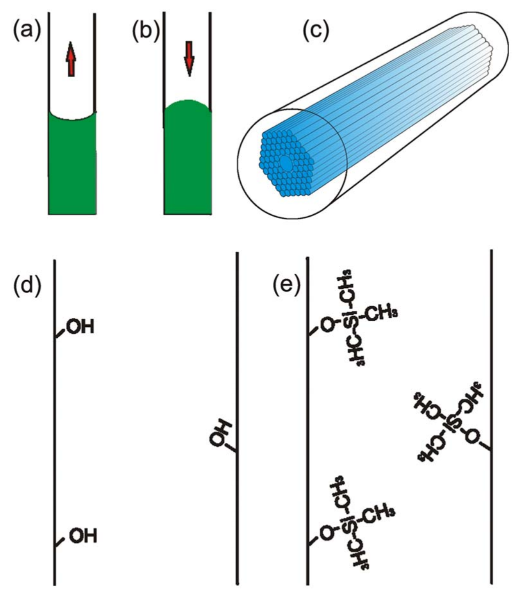

Fig. 1. (Color online) Schematic diagrams of water pulled (a) into a hydrophilic capillary and (b) out of a hydrophobic capillary by capillary forces. (c) Structure of a PCF. (d), (e) Inner surface of a PCF covered with (d) hydroxyl and (e) trimethylsilyl groups.

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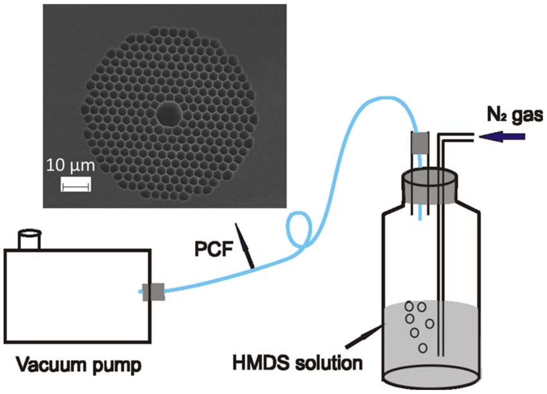

Fig. 2. (Color online) Experimental setup for making PCFs hydrophobic. Inset is a scanning electron micrograph of the cross section of the hollow-core PCF.

except around the molecular absorption peaks. The sensor sensitivity will only be limited at these specified wavelengths of absorption peaks.

To investigate the surface chemistry, the attenuation spectrum of the hydrophobic solid-core PCF was measured (Fig. 3). The three absorption peaks at wavelengths of 1690, 1701, and 1745 nm correspond to C—H stretch resonances and indicate the presence of HMDS-derived trimethylsilyl groups on the silica surfaces [7].

Experiments were conducted to test the water repellent property of the hydrophobic PCFs. Two hollow-core PCFs were aligned, with a small gap in between, using a fusion splicer to observe them microscopically from the side [Fig. 4(a)]. Water from a syringe was injected into the PCF on the right and formed a droplet in the gap [Fig. 4(b)]. The PCF on the left then filled by capillary action; the resultant visible light scattering was readily observed with the white light illumination and the microscope provided with the splicer, in Fig. 4(b). However, when the PCF on the left was hydrophobic [Fig. 4(c)] no visual changes were observed despite several attempts to inject water from the right [Fig. 4(d)]. The hydrophobic PCF was cleaved multiple times and checked at each end, and they all demonstrated good water repellent

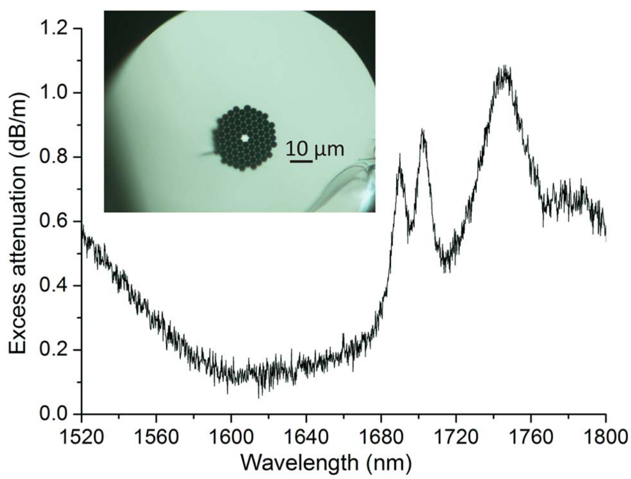

Fig. 3. (Color online) Excess attenuation of a 1 m length of the solid-core PCF due to HMDS surface modification to make it hydrophobic. Inset is a micrograph of the cross section of this PCF.

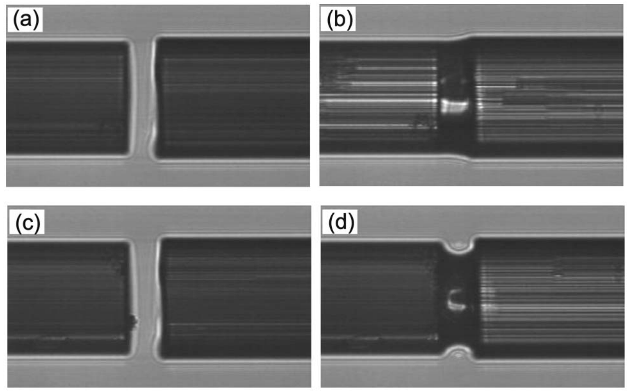

Fig. 4. (a) Alignment of two normal (untreated) hollow-core PCFs. (b) Water from the right-hand PCF was drawn into the PCF on the left. (c) Alignment of a hydrophobic hollow-core PCF on the left and a normal hollow-core PCF on the right. (d) Water was not drawn into the hydrophobic PCF on the left.

properties, indicating that the inner surfaces had been modified all along the length.

We then conducted dissolved-gas sensing experiments using the hydrophobic hollow-core PCF shown in the inset of Fig. 2. 1 m of the fiber was spliced to a conventional single-mode fiber (SMF), which was connected to an erbium-doped fiber amplifier (EDFA) source. The other end of the PCF was immersed in an ammonia solution [Fig. 5(a)]. At various times, this end was taken out from the solution and quickly connected to an optical spectrum analyzer (OSA) to measure the fiber's transmission spectrum [Figs. 5(b) and 5(c)]. The measured absorption resonances from 1525 to 1535 nm match the familiar absorption spectrum of ammonia gas [9]. In contrast, with an untreated PCF, the OSA detected no light at all after the PCF had been immersed in the solution for 3 min, indicating that it had at least partly filled with water and was no longer able to guide light.

Figure 5(b) is the transmission spectrum of the hydrophobic fiber after immersion for various times in the 35 wt. % ammonia solution. The absorption dip increased from 6.1 to 11.1 dB at the strong absorption wavelength of 1531.6 nm when the immersion time increased from 5 to 20 min. With more-dilute 5.2 wt. % ammonia solution, the absorption dip was 0.8 dB at 1531.6 nm after 10 min of immersion [Fig. 5(c)]. The slow response time is not surprising as the free diffusion of gases is very slow from the end of PCFs [10]. However, it can be accelerated by drilling side holes [11] in the PCF before HMDS treatment, which should significantly improve the response time and achieve real-time sensing.

Experiments were also conducted using a different configuration by butt-coupling the end of the hydrophobic PCF with a multimode fiber, leaving a small gap in the solution. We measured transmission spectra through the pair of fibers and achieved similar sensing results. Using the same principle, the hydrophobic PCF can also be used to detect other dissolved gases in water, such as methane and acetylene.

With prior optical dissolved-gas sensing techniques, isolating the sensing part from water was essential because water has broad absorption bands in the IR, severely reducing optical transmission and limiting

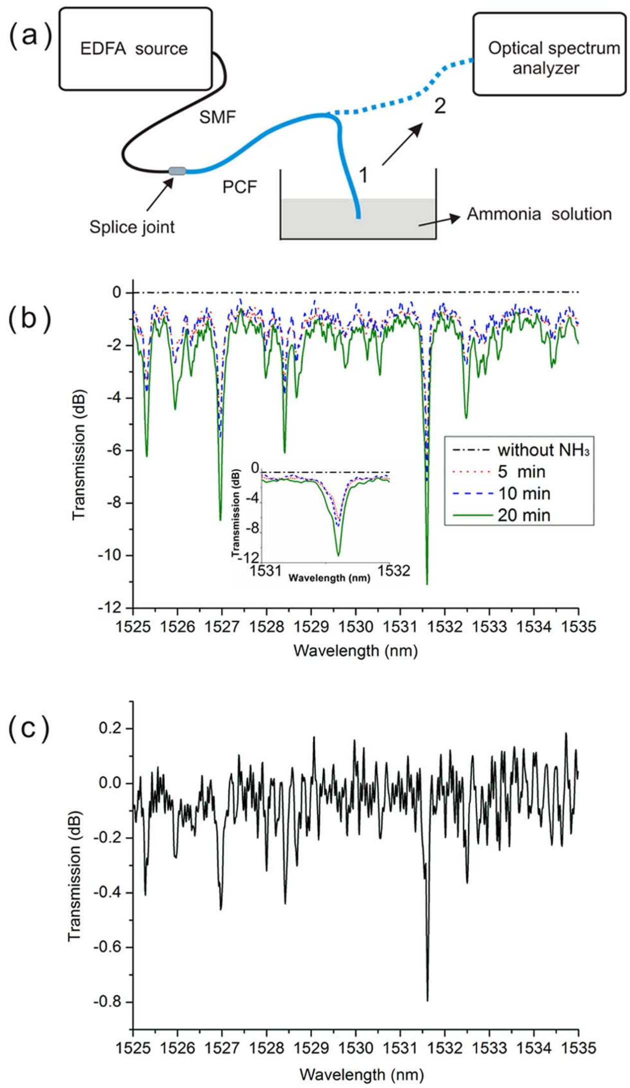

Fig. 5. (Color online) (a) Experimental setup for dissolved-gas sensing. (b), (c) Normalized transmission spectra of a hydrophobic hollow-core PCF exposed (b) for various times to 35 wt. % ammonia solution and (c) for 10 min to a diluted 5.2 wt. % ammonia solution.

sensitivity [12]. The hydrophobic bandgap PCF not only provides the sensing part in the hollow core, but also isolates the water from the inner surfaces of the fiber, thus providing an ultracompact sensing element. It is more sensitive than evanescence-based dissolved-gas fiber sensors [12] because it has a more than 98% overlap of the light with gases in the hollow core. This experiment was conducted in room temperature, but the hydrophobic PCF will work at higher temperatures: indeed, the hydrophobic silica surface treated by HMDS functions at temperatures up to 300 °C [13]. Applications for hydrophobic PCFs should not be limited to dissolved-gas sensing. With its particular properties, it could find other applications, such as optical tweezers [14] in water, the selective filling of PCFs with liquids [15] by the hydrophobic modification of selected holes only, and chemical sensing in aqueous environments.

In conclusion, we have proposed and demonstrated hydrophobic PCFs. We introduced a method for making a PCF hydrophobic, and characterized its properties. The modified inner surfaces of the hydrophobic PCF can repel water without affecting its optical properties, making it useful for operating in an aqueous environment. Dissolved-gas sensing has been demonstrated as an application by using hydrophobic bandgap PCFs in an ammonia solution.

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References

1. J. C. Knight, T. A. Birks, P. St. J. Russell, and D. M. Atkin, Opt. Lett. **21**, 1547 (1996).
2. P. Russell, Science **299**, 358 (2003).
3. P. J. A. Sazio, A. Amezcua-Correa, C. E. Finlayson, J. R. Hayes, T. J. Scheidemantel, N. F. Baril, B. R. Jackson, D. J. Won, F. Zhang, E. R. Margine, V. Gopalan, V. H. Crespi, and J. V. Badding, Science **311**, 1583 (2006).
4. Y. Han, M. K. K. Oo, Y. N. Zhu, L. M. Xiao, M. S. Demokan, W. Jin, and H. Du, Opt. Eng. **47**, 040502 (2008).
5. S. O. Konorov, A. M. Zheltikov, and M. Scalora, Opt. Express **13**, 3454 (2005).
6. P. Domachuk, H. C. Nguyen, B. J. Eggleton, M. Straub, and M. Gu, Appl. Phys. Lett. **84**, 1838 (2004).
7. A. C. Zettlemoyer and H. H. Hsing, J. Colloid Interface Sci. **55**, 637 (1976).
8. L. M. Xiao, M. D. W. Grogan, W. J. Wadsworth, R. England, and T. A. Birks, Opt. Express **19**, 764 (2011).
9. F. Wang, K. F. Cen, N. Li, J. B. Jeffries, Q. X. Huang, J. H. Yan, and Y. Chi, Meas. Sci. Technol. **21**, 045301 (2010).
10. Y. L. Hoo, W. Jin, C. Z. Shi, H. L. Ho, D. N. Wang, and S. C. Ruan, Appl. Opt. **42**, 3509 (2003).
11. A. V. Brakel, C. Grivas, M. N. Petrovich, and D. J. Richardson, Opt. Express **15**, 8731 (2007).
12. C. Boulart, D. P. Connelly, and M. C. Mowlem, Trends Anal. Chem. **29**, 186 (2010).
13. T. J. Ha, H. H. Park, S. B. Jung, H. Ryu, and B. G. Yu, J. Colloid Interface Sci. **326**, 186 (2008).
14. F. Benabid, J. C. Knight, and P. St. J. Russell, Opt. Express **10**, 1195 (2002).
15. L. M. Xiao, W. Jin, M. S. Demokan, H. Ho, Y. Hoo, and C. L. Zhao, Opt. Express **13**, 9014 (2005).